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# Natural attenuation of PAHs under anaerobic conditions

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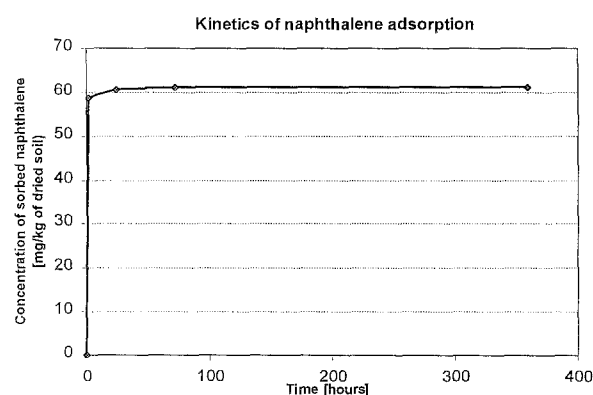
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## 1 Introduction

Risk assessment for groundwater at contaminated sites uses flow and transport modelling. Taking into account the low mobility of PAH's, simulations are carried out for large time scale and natural attenuation, even if low, cannot be discarded. Sensitivity analysis have shown that the integration of biodegradation in the models has a strong effect on the results and on the conclusions of the risk assessment. At the moment, the position of the French Ministry of Environment is close to the position advocated by the Environmental Protection Agency (EPA) in the USA, based on the principle of precaution : "the phenomena of degradation of chemicals can be considered within the risk assessment only if irrefutable evidences of its existence can be brought ".

## 2 Laboratory experiments

Studies have been carried out to check whether natural attenuation of PAH's (mainly sorption and biodegradation) could occur at a disused coke plant site. Two aquifers separated by a clay layer are present at the site location. We performed batch tests in order to measure the partition coefficient of naphthalene on the clay. The kinetics of adsorption are notably fast and the partition coefficient was found to have a value of  $7,64 \text{ cm}^3/\text{g}$ .



picture 1: Kinetics of naphthalene adsorption

We also performed column and microcosm tests in order to check whether biodegradation could occur in the groundwater. A column experiment was performed with soil and groundwater taken from the site. The experimental soil was supplemented with PAH's in the same ratios as found at the source, resulting in a total addition of 200 mg/kg. The soil was then mixed with filter gravel (50 % by volume). The filter gravel increases the hydraulic conductivity and shows nearly no sorption of PAH. The soil was filled into a glass column (10 cm in diameter, 50 cm in length) connected with a reservoir filled with the original groundwater. The water circulated through the soil column from the bottom to the top with the help of a peristaltic pump at a rate of 45 ml/h. The glass reservoirs were wrapped in aluminium foil to avoid photocatalytic degradation. At different time intervals water samples were taken at the sampling port located behind the water reservoir. To ensure anaerobic conditions, the volume of the samples taken was replaced by argon supplied from an argon filled compressible gas bag. After an initial rapid decrease of the concentrations (1<sup>st</sup> to 60<sup>th</sup> day : phase 1), no degradation occurred from the 60<sup>th</sup> to the 100<sup>th</sup> day (phase 2). It is assumed that the first period (1<sup>st</sup> to 60<sup>th</sup> day) is characterised by an adjustment of equilibrium of the PAH concentrations between the soil and the water phase. The decrease of the PAH concentrations initially observed might be due to a slow migration of the pollutants to binding sites on the soil particles (surface and pores). The adaptation of the microflora to the degradation of the PAH under sulfate reducing conditions might have taken about 100 days. Hence, during the 2<sup>nd</sup> phase (60<sup>th</sup> to 100<sup>th</sup> day) no decrease of the PAH concentrations occurred. During the last period (100<sup>th</sup> to 248<sup>th</sup> day : phase 3) degradation of all water-bound PAH took place.

In a first, orientating microcosm experiment, the hypothesis that PAH degradation is linked to sulfate reduction was tested. Three microcosms all containing soil were constructed (abiotic control was achieved by poisoning with HgCl<sub>2</sub>). After an incubation period of 2,5 months, the solid and the liquid phases were separated by centrifugation and the liquid phase only was analysed for its PAH content. The inventory of PAH in the liquid phase was calculated. While the poisoned control exhibited a high residual PAH inventory (1900 µg), only a small amount of PAH (1,1 µg) could be determined in the biotic assay. The inhibition of sulfate reduction by addition of molybdic acid resulted in a significantly higher residual PAH inventory (1180 µg), indicating that the PAH degradation was due to sulfate reduction.

### 3 Modelling

The eventual aim of the research is to achieve best knowledge of sorption and biodegradation rates in order to fit the constants in the modelling. We have already conducted sensitivity analyses that will be included in the paper.

### 4 Literature

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